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Sequential Electrocoagulation- Electrooxidation For Virus Mitigation in Drinking Water

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Highlights

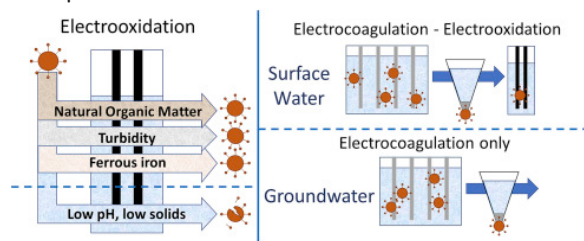
- Ferrous iron impaired, rather than enhanced, electrooxidation for virus treatment.
- Sequential electrocoagulation-electrooxidation was beneficial for surface waters.

- Electrocoagulation alone was preferable for groundwaters.
- Bacteriophages MS2 and Φ X174 overestimated virus reduction compared to echovirus.

Abstract

Electrochemical water treatment is a promising alternative for small-scale and remote water systems that lack operational capacity or convenient access to reagents for chemical coagulation and disinfection. In this study, the mitigation of viruses was investigated using electrocoagulation as a pretreatment prior to electrooxidation treatment using boron-doped diamond electrodes. This research is the first to investigate a sequential electrocoagulation-electrooxidation treatment system for virus removal. Bench-scale, batch reactors were used to evaluate mitigation of viruses in variable water quality via: a) electrooxidation, and b) a sequential electrocoagulation-electrooxidation treatment train. Electrooxidation of two bacteriophages, MS2 and Φ X174, was inhibited by natural organic matter and turbidity, indicating the probable need for pretreatment. However, the electrocoagulation-electrooxidation treatment train was beneficial only in the model surface waters employed. In model groundwaters, electrocoagulation alone was as good or better than the combined electrocoagulation-electrooxidation treatment train. Reduction of human echovirus was significantly lower than one or both bacteriophages in all model waters, though bacteriophage Φ X174 was a more representative surrogate than MS2 in the presence of natural organic matter and turbidity. Compared to conventional treatment by ferric salt coagulant and free chlorine disinfection, the electrocoagulation-electrooxidation system was less effective in model surface waters but more effective in model groundwaters. Sequential electrocoagulation-electrooxidation was beneficial for some applications, though practical considerations may currently outweigh the benefits.

Graphical abstract



Keywords

Bacteriophage, Electrochemical, Disinfection, Echovirus, Inactivation, Iron

1. Introduction

Electrochemical water treatment holds promise as a portable option for coagulation and disinfection in small-scale water systems. More than half of the public water systems in the United States (US) serve fewer than 500 people ([EDR Group, 2013](#)), and approximately 15% of individuals in the US get water from private wells ([DeSimone, 2009](#)). Many of these public and private water systems draw from groundwater and lack disinfection treatment processes. Between 1971 and 2014, over half of the drinking water outbreaks in the US were due to untreated or inadequately treated groundwater ([Centers for Disease Control and Prevention, 2017](#); [Craun et al., 2010](#)).

Electrooxidation (EO) uses inert electrodes to directly oxidize contaminants at the electrode surface and/or generate oxidants in solution. Boron-doped diamond (BDD) electrodes are commonly used in EO research due to BDD's high resistance to chemical and thermal degradation and low tendency to react with solvents ([Macpherson, 2015](#); [Radjenovic and Sedlak, 2015](#)). BDD EO is capable of disinfecting pathogens through either the production of reactive oxygen species (ROS) from electrochemical water decomposition or free chlorine and chlorine dioxide produced from oxidation of chloride ([He et al., 2019](#); [Palmas et al., 2007](#); [Polcaro et al., 2009](#); [Rajab et al., 2015](#)). In the absence of chloride, hydroxyl radicals at the electrode surface are the primary oxidant species, and disinfection relies on pathogen transport and sorption to the electrode surface ([Bruguera-Casamada et al., 2017](#); [Jeong et al., 2006](#)). In general, the efficacy of BDD disinfection increases with the concentration of chloride in the water matrix ([Lacasa et al., 2013](#); [Mascia et al., 2013](#); [Polcaro et al., 2009](#); [Rajab et al., 2015](#)). Increased disinfection in the presence of chloride may indicate that chlorine species are more important to BDD disinfection compared to ROS. Alternatively, chlorine may have a synergistic effect on ROS generation, with more ROS generated in high chloride matrices ([Rajab et al., 2015](#)).

A combined process using EO with BDD followed by electrocoagulation (EC) was used by [Cotillas et al. \(2013\)](#) and [Llanos et al. \(2014\)](#) for *E. coli* mitigation. EC is the *in situ* formation of coagulant in water due to oxidation of a sacrificial anode, typically aluminum or iron. EC has been considered as a pretreatment process for removal of turbidity and natural organic matter (NOM) in a variety of applications ([Bagga et al., 2008](#); [Ben-Sasson et al., 2011](#); [Dubrawski et al., 2013](#); [Vepsäläinen et al., 2009](#)). EC is also an effective means of virus reduction ([Heffron and Mayer, 2016](#)). The primary mechanism of EC is often considered to be the same as chemical coagulation, *i.e.*, physical removal by charge neutralization or sweep flocculation ([Heffron and Mayer, 2016](#)). However, EC can also inactivate viruses and bacteria via generation of free chlorine or Fenton-like reactive intermediates due to ferrous iron oxidation ([Delaire et al., 2015](#); [Heffron et al., 2019a, 2019b](#); [Kim et al., 2011](#); [Tanneru et al., 2014](#); [Zhu et al., 2005](#)). Iron EC generates ferrous ions (Fe^{2+}) in solution by oxidizing a zero-valent iron electrode ([Lakshmanan and Clifford, 2009](#); [Li et al., 2012](#)). The oxidation of ferrous ions to ferric can generate intermediate oxidants capable of inactivating viruses ([Heffron et al., 2019b](#); [Kim et al., 2011](#)). Virus inactivation due to iron EC is more prevalent in slightly acidic waters ($\sim\text{pH } 6$), while physical removal is the dominant fate of viruses in iron EC above $\text{pH } 7$ ([Heffron et al., 2019a](#)). In a combined EO-EC reactor, [Llanos et al. \(2014\)](#) found that iron electrodes were more effective for *E. coli* reduction compared to aluminum electrodes. The team attributed the greater removal observed with iron electrodes to the formation of a passivation layer on aluminum electrodes, though the possibility of *E. coli* inactivation due to iron oxidation was not investigated.

Disinfection by means of EO has been extensively investigated for mitigation of bacteria ([Ahmadi and Wu, 2017](#); [Bruguera-Casamada et al., 2017, 2016](#); [Cossali et al., 2016](#); [Cotillas et al., 2013](#); [Hussain et al., 2014](#); [Lacasa et al., 2013](#); [Rajab et al., 2015](#)), but virus mitigation by EO has received comparatively little attention ([Drees et al., 2003](#); [Fang et al., 2006](#); [Huang et al., 2016](#)). Both bacteriophage MS2 and recombinant human adenovirus have been found to be more resistant to electrochemical disinfection compared to *E. coli* and *Enterococcus* ([Huang et al., 2016](#)). Since bacteria may therefore be poor indicators of virus disinfection via EO, the lack of information on virus mitigation by EO is a critical gap in the literature. Moreover, EC pretreatment ahead of EO may offer advantages for virus treatment, but has not yet been thoroughly assessed.

The goal of this study was to evaluate iron EC as a pretreatment for disinfection of waterborne viruses via BDD EO. To accomplish this goal, the effects of pH, natural organic matter, and turbidity on virus mitigation by EO were first evaluated. The impact of ferrous iron on EO was also investigated in order to design an effective treatment train using sequential EC and EO. Next, a sequential EC-EO treatment train was evaluated for mitigation of two bacteriophage surrogates and echovirus in four synthetic water matrices representing a range of source waters. The EC-EO system was then compared to a more conventional treatment train comprising chemical coagulation and free chlorine disinfection.

Notably, in testing water treatment processes, bacteriophage surrogates are frequently used in place of human viruses for reasons of cost, ease, and safety ([Amarasiri et al., 2017](#); [Boudaud et al., 2012](#); [Ferrer et al., 2013](#); [Grabow, 2001](#)). However, surrogates should be compared to human viruses of interest in any novel application. Echovirus is a ubiquitous pathogen in human-impacted water systems and among the smallest viruses, with diameters typically smaller than 30 nm ([Grabow, 2007](#); [World Health Organization, 1996](#)). Previous research ([Heffron et al., 2019a](#)) has determined that echovirus 12 is resistant to inactivation by EC and is therefore a conservative indicator of virus mitigation.

2. Materials and methods

2.1. Batch electrocoagulation and electrooxidation process operation

All EC and EO tests were conducted in 200-mL polypropylene batch reactors. EC reactors utilized four 1020 steel electrodes (VMetals, Milwaukee, WI). EO reactors used a single BDD/Si anode (NeoCoat SA, La Chaux-de-Fonds, France) and commercially available pure Grade 2 titanium as an inert cathode (Performance Titanium Group, San Diego CA). Similar disinfection performance may be possible with lower cost electrodes, for example graphite ([Hussain et al., 2014](#); [Saha and Gupta, 2017](#)). However, BDD electrodes were used in this study as a representative EO treatment because of the prevalence of BDD usage in electrochemical disinfection research. The BDD coating was 3 μm thick and p-doped with 700–800 ppm boron. All electrodes had a submerged working surface area of 15 cm^2 (5 cm \times 3 cm).

Prior to use, iron EC electrodes were wet-polished with 400 grit Si-C sandpaper, triple-rinsed with PureLab ultrapure water (ELGA LabWater, UK), and then disinfected under UV light for 30 min per side in a biosafety cabinet. EC electrodes were polarized at 100 mA in 3 mM sodium bicarbonate solution for 10 min to mimic conditions of continual use in drinking water, then thoroughly rinsed with ultrapure water to remove residual iron. The BDD anode and titanium cathode were polarized at 100 mA for 10 min in 0.1 M H_2SO_4 to rehydrogenize the electrode surface before each test in order to provide consistent electrode conditions ([Jeong et al., 2006](#); [Macpherson, 2015](#)).

2.2. Virus propagation and quantification

Two bacteriophages were used as human virus surrogates: MS2 (ATCC #15597-B1) and ΦX174 (ATCC #13706-B1). MS2 is an F-specific coliphage with a single-stranded RNA genome (Baltimore group IV), while ΦX174 is a somatic coliphage with a single-stranded DNA genome (Baltimore group II) ([Grabow, 2001](#)). These bacteriophages are standard laboratory surrogates for enteric viruses ([Heffron and Mayer, 2016](#)). To evaluate the suitability of these bacteriophage surrogates for indicating human virus mitigation during electrochemical treatment, human echovirus 12 (ATCC #VR-1563) was used to verify a subset of tests.

Bacteriophages were propagated using the double-agar layer (DAL) method. *E. coli* ATCC #15597 and #13706 were used to propagate and quantify MS2 and ΦX174, respectively. Echovirus was propagated in Buffalo Green Monkey Kidney cell culture (ATCC CCL-161) until cell monolayers were reduced to approximately 10–20% confluence, then subjected to three freeze-thaw cycles at –20 °C. All viruses were purified by two cycles of polyethylene glycol (PEG) precipitation followed by a Vertrel XF (DuPont, Wilmington, DE) purification, as described by [Mayer et al. \(2008\)](#). Bacteriophages were quantified using the spot titer plaque assay method, as described by [Beck et al. \(2009\)](#). Echovirus was quantified using the Reed & Muench TCID₅₀ method ([Reed and Muench, 1938](#)). Bacteriophages were stored at 4 °C. Even at low concentrations, dimethyl sulfoxide (DMSO) inhibited bacteriophage inactivation due to EO, as shown in the Supporting Information (SI) 1. DMSO exerts a high demand for hydroxyl radicals at concentrations as low as 0.25 mM ([Tai et al., 2004](#)). For this reason, echovirus was stored at –20 °C without cryopreservant and was used within 2 months of propagation.

Bacteriophages were spiked at concentrations of approximately 10⁷ PFU/mL, while echovirus was spiked at approximately 10⁴ TCID₅₀/mL due to limitations in virus propagation. After treatment, the reactor was briefly homogenized by rapid stirring (600 rpm for 15 s), and a 20-mL sample was taken for virus elution. Elution was performed 15 min after EO treatment to allow the same reaction time as EC. Elution was performed by adding an equal volume of 6% beef broth to homogenized samples and vortexing for approximately 10 s. Samples containing bacteriophages were diluted in tenfold series in pH 7.0 buffered demand free (BDF) water, and ten 10-μL drops of each dilution were plated. Samples containing echovirus were also diluted in BDF. Aliquots of 100 μL from each echovirus dilution series were added to 6 wells in a 24-well tray of 1-day-old BGM cells. BGM cultures were observed under magnification for the appearance of cytopathic effects over the following 10 days, and were quantified using the Reed & Muench TCID₅₀ method ([Reed and Muench, 1938](#)).

2.3. Impact of water constituents on electrooxidation

To test the impact of NOM, turbidity, pH, and ferrous iron on EO with BDD electrodes, batch EO tests were performed at a constant current of 20 mA ($i = 1.3 \text{ mA/cm}^2$) for 5 min. Sodium bicarbonate (2.1 mM) was added to ultrapure water for a background electrolyte solution, and pH was adjusted with 1 M H₂SO₄ or NaOH. NOM, turbidity, and ferrous iron tests were conducted at pH 7; pH tests were conducted at pH 6, 7, and 8. NOM was added as humic acid sodium salt (Sigma Aldrich, St. Louis, MO) at concentrations of 0.1–15 mg/L total organic carbon (TOC). Turbidity was increased by adding A2 test dust (Powder Technology Inc., Arden Hills, MN) to approximately 1–30 NTU. Contributions of NOM to TOC were measured using a TOC-V CSN total organic carbon analyser (Shimadzu, Kyoto, Japan) following sample acidification with analytical grade hydrochloric acid. Though NOM contributes to turbidity, tests were performed by adding enough A2 dust to provide the target turbidity (see SI 2) independent of NOM. Turbidity was measured using a Hach 2100AN Turbidimeter (Hach, Loveland, CO).

2.4. Sequential electrocoagulation-electrooxidation process operation

A treatment train schematic for sequential EC-EO treatment is shown in [Fig. 1](#). Preliminary testing determined that a particle separation step between the EC and EO stages provided greater bacteriophage reduction, as shown in SI 3. For this reason, the entire volume of the reactor was filtered before EO treatment with a Whatman 114 filter to remove coarse precipitates (>25 μm) without affecting turbidity or NOM. Due to potential formation of iron flocs from dissolved iron during EO treatment, an additional filtration step was performed after EO as well. After final filtration, 5-mL

samples were diluted into 5 mL 6% beef broth (pH 9.5) to elute viruses from any remaining floc and promote monodispersion.

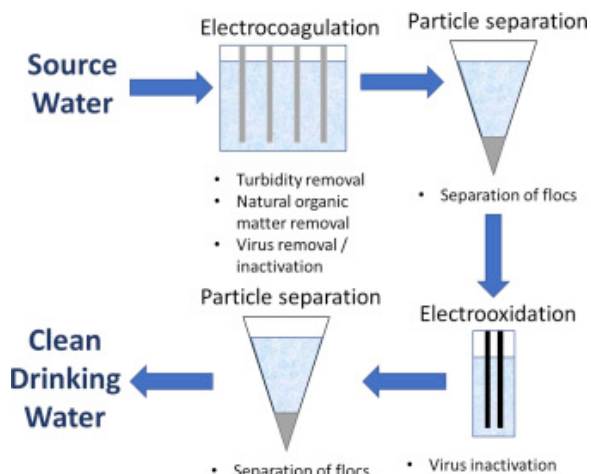


Fig. 1. Schematic of electrocoagulation-electrooxidation treatment train and hypothesized treatment effects for each stage.

Untreated controls were performed along with every EC-EO treatment test. All untreated controls were retained in reactors for the same amount of time as treated replicates (but without electrochemical treatment) and underwent the same filtration and elution procedures. Log reduction of viruses was calculated by comparing eluted virus concentrations after EC-EO to these untreated controls. Therefore, these controls accounted for any minor losses of virus due to sorption to the coarse filters or elution. The data indicated that virus concentrations remained at approximately the spiked concentration in the untreated controls (10^7 PFU/mL for bacteriophages and 10^4 TCID₅₀/mL for echovirus), indicating that any virus loss due to experimental artifact was minor. In combination with floc formation, some fraction of viruses was expected to be retained with the floc on the coarse filter. In any coagulation process, some method of floc separation is required, whether settling, centrifugation or filtration. In this case, a coarse filter was used for expediency compared to gravitational separation and to provide a more conservative account of physical separation compared to microfiltration.

A constant charge loading of 150 C/L was divided between the EC and EO processes by varying current over a constant retention time of 5 min per treatment process. The charge loading of 150 C/L (50 mA applied over 10 min total reaction time in a 200 mL reactor, $i_{EC} = 1.1$ mA/cm², $i_{EO} = 3.3$ mA/cm²) was chosen in order to establish a curve that demonstrated differences between charge allocations and virus log reduction without exceeding the measurable limit of virus reduction (~5 log reduction), as explained in SI 4. Total and ferrous iron concentrations were measured using Hach FerroVer Total Iron and Ferrous Iron Reagent (Hach, Loveland, CO). Absorbance was measured at 510 nm using a Genesys 20 spectrophotometer (Thermo Fisher Scientific, Waltham, MA).

2.5. Preparation of synthetic waters for sequential EC-EO process

Removal of the two bacteriophage surrogates (MS2 and ΦX174) and echovirus was evaluated in synthetic waters modeled after a range of environmental source waters. Four model waters were synthesized by adding reagent-grade chemicals to ultrapure water and adjusting pH, NOM, and turbidity, as shown in [Table 1](#). Model water parameters were based on water quality data for the Mississippi River at Brooklyn Park, MN, Lake Michigan at Milwaukee, WI, and shallow (dolomite), and

deep (sandstone) aquifers near Lincoln township and Waukesha, WI, as detailed in SI 2. To represent the anoxic conditions of groundwater, Dolomite and Sandstone Aquifer model waters were degassed using argon for 15 min prior to pH adjustment and virus addition.

Table 1. Model water parameters.

Water Matrix	Alkalinity (mg/L as CaCO ₃)	Chloride (mg/L)	Added Turbidity (NTU)	Total Organic Carbon (mg/L)	pH	Conductivity (µS/cm)	Dissolved Oxygen (mg/L)
Lake Michigan	118	13	0	2	8.3	340	9
Mississippi River	162	11	30	8.7	8.1	400	9
Sandstone (deep) Aquifer	220	4	0	0	7.5	550	0.3
Dolomite (shallow) Aquifer	320	70	10	0	7.5	1000	0.4

2.6. Comparison of sequential EC-EO to conventional coagulation/disinfection

Ferric chloride was added to match the iron dose achieved by 50 mA EC with a 5-min retention time (22 mg Fe/L) to represent a 50/50 allocation of charge for EC-EO. Reactors were rapidly stirred (600 rpm) for 30 s, followed by a slower stir rate (200 rpm, as used in EC) for 270 s (total reaction time of 5 min). Consistent with EC-EO treatment tests, reactors were allowed to settle for 15 min without stirring, and then the total volume was passed through a Whatman 114 filter. Sodium hypochlorite was added (1.2 mg/L as Cl₂, 5 min retention) to meet the recommended 6 mg-min/L chlorine dose for small water treatment systems ([Washington Administrative Code, 2017](#)). After 5 min retention time, an excess of sodium thiosulfate (0.03 mM) was added to the reactor to quench residual chlorine.

2.7. Data analysis

All statistical analyses were performed in the R statistical language using the stats package ([R Core Team, 2014](#)). Bacteriophage inactivation was correlated to charge allocation between EC and EO by linear regression. Models were evaluated for residual distribution, normality, and leverage points (Cook's distance) using the plot.lm() function, and significance of variables was evaluated by analysis of variance with the anova() function ([R Core Team, 2014](#)). Akaike's 'An Information Criterion' was used to evaluate the goodness-of-fit and parsimony of competing linear models ([R Core Team, 2014](#); [Sakamoto et al., 1986](#)).

Echovirus tests were performed in triplicate at 0, 50, and 100% charge allocations to EC and compared to MS2 and ΦX174 reduction in the same waters at all charge allocations. One-way ANOVA was performed to assess differences in mean removal between viruses within each model water. Post-hoc comparison of means was performed using Tukey's HSD using the aov() and TukeyHSD() functions ([R Core Team, 2014](#)).

The electrical energy per order of magnitude (EEO, [Bolton et al., 1996](#)) virus reduction was calculated for the sequential EC-EO treatment in the four model waters. This parameter provides a benchmark for comparing the energy costs of virus mitigation in different treatment scenarios.

3. Results and discussion

3.1. Effect of water constituents on BDD electrooxidation

To evaluate the impact of water quality on virus inactivation via EO, BDD EO was performed under conditions of varying NOM, turbidity, and pH. Both NOM and turbidity impeded EO, as shown in [Fig. 2](#). NOM increases oxidant demand, resulting in poorer disinfection of target pathogens ([Haselow et al., 2003](#)). NOM is particularly effective at quenching hydroxyl radicals, with a rate constant near $10^8 \text{ M}^{-1}\text{s}^{-1}$ ([Westerhoff et al., 2007](#)). Hydrophobic virions may also sorb to, and be shielded by, NOM. The A2 test dust used to increase turbidity consists of silica, alumina, and various metal oxides ([Powder Technology Inc., 2016](#)). The presence of metal oxides in A2 test dust likely provides oxidant demand, leading to the poor inactivation shown in [Fig. 2B](#). Therefore, a pretreatment stage prior to EO is needed to mitigate the negative influence of NOM and turbidity on virus inactivation during EO.

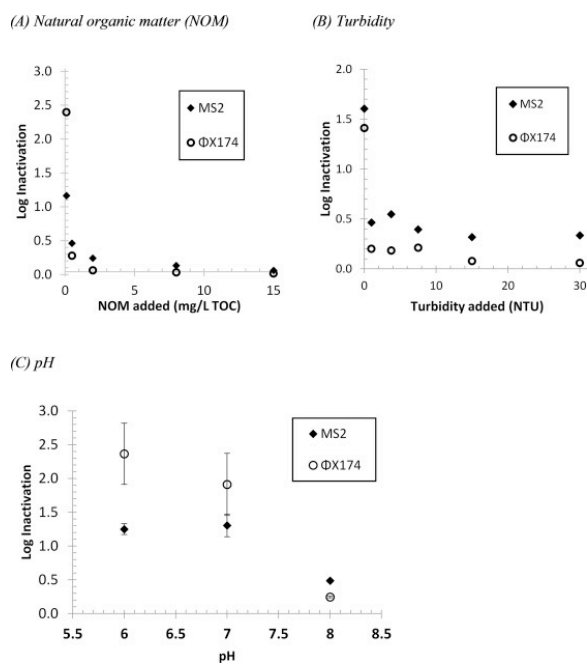


Fig. 2. Impact of water quality, (A) natural organic matter, (B) turbidity, and (C) pH, on bacteriophage MS2 and ΦX174 reduction by electrooxidation using boron-doped diamond (BDD) electrodes (20 mA, 5 min). Tests were conducted in 2.1 mM NaHCO_3 . Both NOM and turbidity inhibited inactivation, and inactivation was significantly lower at pH 8. Points in [Fig. 2A](#) and B represent single tests (mean of 10 counts). In [Fig. 2C](#), points represent mean values of triplicate tests with ± 1 standard error shown by the error bars.

Reduction of both MS2 and ΦX174 was greater at pH 6 and 7 compared to pH 8, as shown in [Fig. 2C](#). Generation of ROS (primarily hydroxyl radicals) due to EO is greater at lower pH ([Jeong et al., 2006](#)). Inactivation of either bacteriophage was not statistically different between triplicate tests at pH 6 and 7. Therefore, virus reduction above pH 7 should be a conservative indicator of reduction in slightly acidic waters as well. For this reason, model waters below pH 7 were not investigated in later experiments. In all tests, pH increased slightly during the EO process by an average of 0.20 ± 0.05 pH units.

3.2. Impact of ferrous iron on BDD electrooxidation

In addition to directly oxidizing contaminants, ferrous iron can enhance other oxidation treatment processes. Iron-enhanced oxidation has been demonstrated for many contaminants. Ferrous-catalyzed ozonation has been found to be more effective than ozonation alone in oxidizing organic pollutants and COD ([Arslan-Alaton, 2001](#); [Beltrán et al., 2005](#); [Legube and Karpel Vel Leitner, 1999](#)). Researchers have found that ferric iron has similar, albeit possibly lesser, catalytic effects for ozonation of organic pollutants ([Beltrán et al., 2005](#); [Sreethawong and Chavadej, 2008](#)). Though disinfection studies using iron-enhanced oxidation are scarce, [Sjogren and Sierka \(1994\)](#) found that 2 μM ferrous sulfate-augmented TiO_2 photocatalysis achieved an additional 2 \log_{10} reduction of MS2 over TiO_2 photocatalysis alone. Although the mechanisms for enhancing oxidation are likely different between these treatment processes and BDD EO, iron enhancement is common among these processes. To the authors' knowledge, iron-enhanced BDD EO has not previously been investigated. Using an oxidation method like EO could also regulate iron oxidation to maximize disinfection and minimize soluble iron residuals. Conversely, EO may benefit EC by further oxidizing iron species to form more floc.

For this reason, the possible synergistic effects of ferrous iron generated by EC and EO performance was investigated. As shown in SI 3, inclusion of a filtration step between EC and EO improved virus reduction beyond EC alone. Thus, ferrous iron from EC likely created an oxidant demand rather than enhancing EO. To confirm the effect of ferrous iron as an oxidant scavenger, a follow up experiment was performed using ferrous chloride to demonstrate the effect of ferrous iron dose on EO inactivation. Samples of the bulk solution after EO were homogenized and eluted (6% beef broth, pH 9.5) to show the effect of inactivation only, without considering removal due to coagulation/destabilization. As shown in [Fig. 3](#), the oxidant demand of ferrous iron inhibited virus inactivation at low doses. At higher doses of ferrous iron, virus inactivation eventually met or exceeded the level achieved by EO without ferrous addition. Therefore, ferrous iron may catalyze virus inactivation, but the concentration of iron needed ($>30 \text{ mg/L Fe}$) to do so may be cost-prohibitive and introduce high concentrations of residual iron. Based on these observations, one innovation of our study was to use a sequential EC-EO process and to include a separation step to remove iron precipitate prior to EO. Previous attempts to combine iron EC and EO processes have used a simultaneous EC/EO reactor that would likely be inhibited by the oxidant demand of ferrous iron ([Llanos et al., 2014](#)).

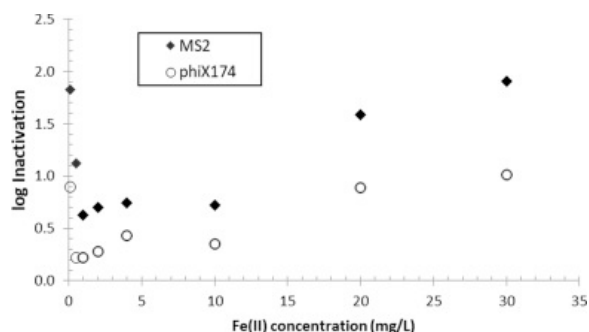


Fig. 3. Combined effect of ferrous chloride coagulation and subsequent boron-doped diamond electrooxidation on the reduction of bacteriophages MS2 and ΦX174 . Inactivation was inhibited by low doses of ferrous iron and returned to iron-free inactivation levels only at very high doses ($\sim 30 \text{ mg/L Fe}$). Tests were conducted in 2.1 mM NaHCO_3 , pH 7. Points represent single tests (mean of 10 counts).

3.3. Sequential EC-EO treatment of model waters

3.3.1. Charge allocation for optimal EC-EO virus mitigation

The impact of energy allocation between EC and EO in the EC-EO treatment train was evaluated to determine how the two processes might be balanced for enhanced virus reduction. The total charge loading of 150 C/L for EC-EO treatment and retention time of 5 min per process were held constant while current allocated to each treatment varied. Increased charge allocation to EC from 0% to 100% (0–100 mA) was approximately equal to the increase in energy density (kWh/m³, or energy normalized to the reactor volume) for EC and EO, as shown in SI 5. Here, virus mitigation was related to charge allocation so that the results could be generalized to other EC and EO reactors. These charge allocation tests were conducted in each of the four model waters representing a wide range of environmental source waters (summarized in [Table 1](#)).

The effect of charge allocation on MS2 and ΦX174 bacteriophage removal is shown in [Fig. 4](#) for the four model waters. Charge allocation was arbitrarily represented as a percentage of the total charge loading allocated to EC. Regression models expressing log reduction in terms of percent charge allocated to EC are summarized in [Table 2](#), including estimated optimal charge allocation in each source water. Both surface waters (Lake Michigan and Mississippi River) tended to favor the dual process of EC-EO, with optimal charge allocated to EC of 47% (both MS2 and ΦX174) in Lake Michigan model water and 60% (MS2) or 26% (ΦX174) in Mississippi River model water. Sandstone Aquifer model groundwater favored EC alone, while Dolomite Aquifer model groundwater showed no significant trend, with similar removal across the charge allocation range. The main difference in formulation between these two waters was the chloride concentration (see [Table 1](#)), with Sandstone Aquifer comprising very little chloride (4 mg/L Cl⁻) and Dolomite an excess of chloride (70 mg/L Cl⁻). Evolution of free chlorine was therefore likely to have improved disinfection by EO, as previous researchers have also reported ([Lacasa et al., 2013](#); [Mascia et al., 2013](#); [Polcaro et al., 2009](#); [Rajab et al., 2015](#)). Nevertheless, EO still did not surpass EC in Dolomite Aquifer model water.

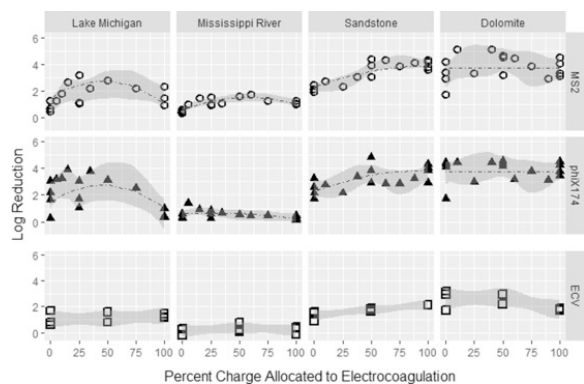


Fig. 4. The effect of charge allocation between iron electrocoagulation and boron-doped diamond electrooxidation on the reduction of bacteriophages MS2 and ΦX174 and human echovirus 12 (ECV) in four model waters. Poorest removal occurred in Mississippi River water (the highest in NOM and turbidity), while greatest average removal occurred in Dolomite Aquifer (the highest in conductivity and chloride). Points represent single tests (mean of 10 counts for bacteriophages, single well plates for ECV); lines represent predicted values based on regression models. ECV data was insufficient to characterize over the entire range of charge allocation.

Table 2. Summary of linear regression models for log reduction of bacteriophage MS2 and ΦX174 as a function of the percent of the total charge used in the EC-EO treatment process (150 C/L) that was allocated to EC (“% EC”). Estimated optimal charge allocation based on the regression models ranged from 26% to 100% EC. A single model described log reduction of both MS2 and ΦX174 for all waters except Mississippi River. Log reduction in the Dolomite Aquifer model water was independent of charge allocation, so there was no optimal % EC.

		Lake Michigan		Mississippi River		Sandstone Aquifer		Dolomite Aquifer	
		MS2	ΦX174	MS2	ΦX174	MS2	ΦX174	MS2	ΦX174
Intercept	β	1.46		0.584	0.584	2.28		3.53	
	p-value	2.04E-05		1.50E-07	1.50E-07	2.24E-13		<2e-16	
% EC	β	0.0557		0.0313	0.00438	0.0329		n.s	
	p-value	5.21E-03		1.49E-05	5.72E-04	1.39E-03		n.s	
(% EC) ²	β	-5.96E-04		-2.63E-04	-7.62E-05	-1.74E-04		n.s	
	p-value	2.24E-03		2.00E-04	2.39E-02	6.32E-02 ^a		n.s	
Estimated optimal % EC		47%		60%	26%	100%		N/A	
F statistic (degrees of freedom)		6.047 (2,29)		14.28 (4, 27)		20.15 (2,31)		N/A	
R ² _{adj}		0.25		0.63		0.54		N/A	

n.s: Not significant.

N/A: Not applicable as log reduction was independent of charge allocation.

^aVariable was not strictly significant ($\alpha = 0.05$) but was determined to be beneficial to the model by Aikake's An Information Criterion (AIC).

This trend was somewhat surprising because model groundwaters had a lower pH (pH 7.5) than surface waters (pH 8.1–8.25). During the EC-EO process, pH increased slightly in all model waters but did not increase disproportionately for surface waters, as shown in SI 5. Therefore, EO was expected to be more effective in groundwaters than surface waters. In fact, log reduction was overall greater in groundwaters. This indicates that low pH improved virus mitigation via EC to an even greater extent than EO. Previous research ([Heffron et al., 2019a](#)) has demonstrated that inactivation via iron EC increases at lower pH levels and may even become the dominant fate of viruses. Bacteriophage inactivation is a function of both the amount of iron oxidation and the iron oxidation rate ([Heffron et al., 2019b](#)). Because the groundwaters had low initial pH and dissolved oxygen concentrations, greater ferrous concentrations were maintained in solution, as shown in SI 6. In low-oxygen conditions, ferrous iron requires a longer time to oxidize ([Stumm and Lee, 1961](#)). Therefore, model groundwaters offered a more favorable environment for virus inactivation due to ferrous iron.

As anticipated, the high NOM, high turbidity, and high pH Mississippi River water was the most challenging for virus reduction. Ferrous iron binds with NOM, thereby becoming resistant to oxidation ([Crittenden et al., 2012](#)). Accordingly, ferrous iron residual remained high after EO only in the high-NOM

Mississippi River water (see SI 6). Therefore, NOM impairs not only the EO stage ([Fig. 3](#)), but also EC. The failure of EC to dramatically improve virus mitigation in Mississippi River water is testament to the fact that EC did not substantially improve water quality prior to EO (in contrast to the original hypothesis). In Mississippi River water, total organic carbon did not significantly change between the initial concentration and post-EO filtration ($p = 0.175$). Decreasing pH prior to EC to achieve enhanced coagulation can improve NOM removal ([Vepsäläinen et al., 2009](#)). However, the tendency of EC to increase solution pH could counteract enhanced coagulation.

The electrical energy per order (EEO) for virus reduction further highlighted the efficacy of the overall treatment in model groundwaters over model surface waters, as shown in [Fig. 5](#). In a sequential treatment evenly divided between EC and EO (50 mA for 5 min in each stage), log virus reduction required approximately 2–10 times greater energy input in model surface waters compared to groundwaters. The greater energy density requirements are due not only to poorer virus mitigation in surface waters, but also the higher potentials needed to overcome resistance due to low conductivity (see [Table 1](#)). Though EEO provides a benchmark for comparing virus mitigation in the different model water matrices used in this study, using EEO to compare to other technologies is potentially problematic. The batch EC and EO reactors used in this study were not optimized for energy efficiency, so comparisons to established technologies are not possible. In addition, a lack of standard experimental conditions for assessing EEO makes comparisons between even studies using the same technology problematic ([Litter et al., 2018](#)). With these caveats in mind, it is still possible to compare the order of magnitude of EEOs in this study to other values. An EEO of $<0.265 \text{ kWh/m}^3$ is generally recommended, although higher values have been used in cases where there are no treatment alternatives ([Crittenden et al., 2012](#)). [Fig. 5](#) shows that groundwater treatment using EC-EO for virus mitigation falls within the recommended range, even without any attempt to optimize the process for power efficiency.

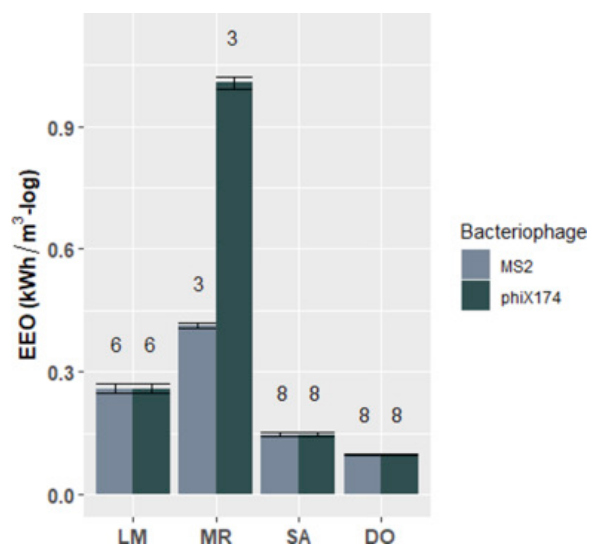


Fig. 5. Electrical energy per order (EEO) for the sequential electrocoagulation – electrooxidation treatment train in four model waters. Though the batch reactors used in this study were not optimized for energy efficiency, EEO provides a benchmark for comparing the energy cost of virus mitigation between different water matrices. Log reduction was estimated in each water for an even distribution of charge between electrocoagulation and electrooxidation (50 mA for 5 min, or 75 C/L, per process) using the regression models shown in [Table 2](#). LM = Lake Michigan, MR = Mississippi River, SA = Sandstone

Aquifer, and DO = Dolomite Aquifer model waters. Each column represents the mean values of replicate tests (n shown above bars) with ± 1 standard error shown by the error bars.

Though the trends modeled in [Fig. 4](#) were significant, triplicate tests of virus mitigation did not significantly differ between a balance of EC-EO and EC alone. These results indicated that EC alone was nearly as effective as the sequential EC-EO treatment. Ferrous iron concentrations entering the EO stage were low (0.02–0.17 mg/L Fe, see SI 6), but still in the inhibitory range for EO ([Fig. 3](#)). Therefore, a more effective particle separation stage, *e.g.*, microfiltration, could lead to greater disinfection in the EO stage. Given the relative cost of iron and BDD electrodes, a one-stage EC treatment would be far preferable for virus mitigation from a practical standpoint. In addition, the combination of ROS and chlorine species formed by BDD electrodes can give rise to disinfection byproducts (DBPs) like chlorate and perchlorate unless operating conditions are carefully controlled ([Polcaro et al., 2009](#); [Rajab et al., 2015](#)). However, EO may still offer benefits for oxidizing other contaminants, such as organic micropollutants. EO also oxidized residual ferrous iron after EC for most waters (see SI 6). EO can therefore act as a polishing step to oxidize residual iron for improved precipitation and removal in order to meet aesthetic standards for iron in drinking water.

3.3.2. Comparison of bacteriophage surrogates to human echovirus 12

Reduction of echovirus by the EC-EO treatment train was also evaluated in the four model waters, as shown in [Fig. 4](#). Echovirus mitigation followed the same pattern as bacteriophages, in order of increasing reduction: Mississippi River < Lake Michigan < Sandstone Aquifer \approx Dolomite Aquifer (as summarized in SI 2). However, the mean reduction of echovirus was significantly less than one or both bacteriophage surrogates in all model waters by a factor of 0.9–1.5 logs, as summarized in [Table 3](#). By contrast, the two bacteriophages significantly differed only in Mississippi River model water, where removal followed the pattern of echovirus \approx Φ X174 < MS2.

Table 3. Comparison of bacteriophage surrogates MS2 and Φ X174 and human echovirus 12 (ECV) reduction due to sequential electrocoagulation-electrooxidation treatment. Mean reduction from all tests in each model water was compared by Tukey's HSD. Entries in bold indicate significant differences ($\alpha = 0.05$).

Water Matrix	Mean Difference in Log Reduction and Significance (Adjusted p-value)		
	MS2 - ECV	Φ X174 - ECV	MS2 - Φ X174
Lake Michigan	0.660	1.266	-0.606
	<i>p</i> = 2.53E-01	<i>p</i> = 9.73E-03	<i>p</i> = 1.69E-01
Mississippi River	0.876	0.420	0.457
	<i>p</i> = 1.76E-05	<i>p</i> = 4.59E-02	<i>p</i> = 4.72E-03
Sandstone Aquifer	1.503	1.334	0.169
	<i>p</i> = 2.58E-05	<i>p</i> = 1.64E-04	<i>p</i> = 7.57E-01
Dolomite Aquifer	1.092	1.213	-0.122
	<i>p</i> = 2.27E-02	<i>p</i> = 1.02E-02	<i>p</i> = 9.20E-01

Mitigation of bacteriophage MS2 was significantly higher in Mississippi River model water than either Φ X174 or echovirus, which indicates that bacteriophage Φ X174 mitigation is impaired to a greater degree by NOM and turbidity. As discussed in Section [3.1](#), NOM and turbidity can dramatically impact

the efficacy of EO. NOM also impairs virus mitigation by iron EC ([Heffron et al., 2019a](#); [Tanneru and Chellam, 2012](#)). Though neither phage was a conservative surrogate, the lack of a significant difference in echovirus and ΦX174 mitigation in Mississippi River model water indicates that ΦX174 should be considered the more conservative surrogate for human viruses across a range of waters. In addition, the difference in mean log reduction between bacteriophage ΦX174 and echovirus was consistent across model waters (between 2 and 3 times greater log reduction). Until a better surrogate is identified, correcting bacteriophage ΦX174 inactivation results by a safety factor of 2-log reduction could provide a reasonable indicator of echovirus mitigation.

3.3.3. Comparison to conventional coagulation/disinfection

The EC-EO treatment train was compared to a conventional treatment train of chemical coagulation with ferric chloride salt (22 mg Fe/L, equivalent to the iron generated by EC at 50 mA for 5 min) and free chlorine (1.2 mg/L Cl₂). The purpose of this comparison was to evaluate the relative efficacy of EC-EO compared to typical treatment processes under identical water quality conditions. Although the iron dose was equivalent to the EC dose for Dolomite Aquifer and Sandstone Aquifer model groundwaters, these tests did not provide a mechanistic comparison to the conventional treatment train as they did not account for ferrous oxidation, generation of ROS, or anodic oxidation.

In the Lake Michigan and Mississippi River model surface waters, the conventional treatment system outperformed the EC-EO system, as shown in [Fig. 6](#). However, in the model Sandstone and Dolomite Aquifer groundwaters, EC-EO dramatically outperformed the conventional system. This discrepancy may be due to iron-based disinfection in low-oxygen waters, as discussed in [Section 3.3.1](#). In addition, the two surface waters were above pH 8, leading to poor conditions for disinfection by either free chlorine or hydroxyl radicals. Addition of chemical coagulant decreased the pH to 7.0 or less in all waters, which likely improved disinfection by ensuring free chlorine was predominately in the hypochlorous acid, rather than the hypochlorite, form.

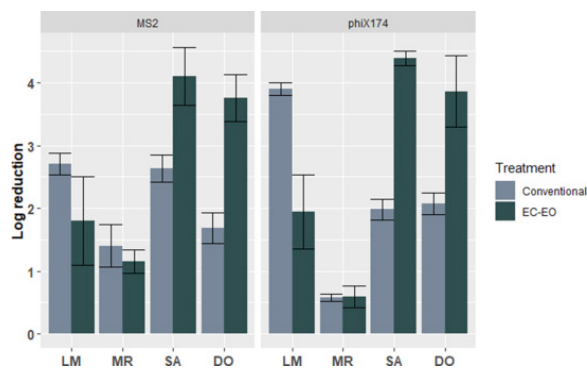


Fig. 6. Comparison of conventional coagulation/chlorination treatment train to the electrocoagulation-electrooxidation (EC-EO) treatment train for the reduction of bacteriophages MS2 and ΦX174.

“Conventional” treatment consisted of FeCl₃ chemical coagulation (22 mg/L Fe) followed by NaOCl disinfection (6 mg-min/L Cl₂). EC-EO was conducted near the optimal division of 150 C/L in the EC-EO treatment train (25% EC for LM and MR, 50% EC for DO and SA). LM = Lake Michigan, MR = Mississippi River, SA = Sandstone Aquifer, and DO = Dolomite Aquifer model waters. Each column represents the mean values of triplicate tests with ±1 standard error shown by the error bars.

Even when conventional treatment outperforms EC-EO, logistical considerations may favor one water treatment train over the other. On one hand, the EC-EO treatment system requires further power

optimization to be feasible for large-scale surface water applications. On the other, the system's portability, potential for automation, and lack of caustic chemical additions make EC-EO a viable option for small-scale, distributed treatment. The cost of BDD electrodes is a major hurdle to implementing an EC-EO treatment process. However, EO may provide other benefits not considered here, e.g., the oxidation of organic micropollutants or residual iron from EC treatment. As new, more cost-effective EO electrodes are developed, the combined EC-EO process will become more attractive as an alternative to conventional drinking water treatment.

4. Conclusions

Few studies have assessed EC and EO individually for virus mitigation, and no previous research has investigated an EC-EO process for virus mitigation. This study both establishes a basis for using a novel, sequential EC-EO treatment train for drinking water and thoroughly evaluates treatment performance for two bacteriophages and a human waterborne virus. Neither bacteriophage was a conservative surrogate for human echovirus, although ΦX174 was a better predictor of echovirus mitigation.

Though the EC-EO treatment system proposed in this study was not beneficial in all water matrices, the improved virus mitigation achieved by EC-EO in model surface waters warrants further attention. The benefit of EC-EO was probably not due to iron-enhanced oxidation. Instead, greater virus reduction observed in the EC-EO treatment train was likely achieved by the additive effects of physical removal via coagulation/filtration, ferrous iron-based disinfection, and EO disinfection.

Acknowledgments

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Appendix A. Supplementary data

The following is the Supplementary data to this article:

Sequential electrocoagulation-electrooxidation for virus mitigation in drinking water

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The supporting information consists of 12 pages, including 6 sections, 1 table, and 7 figures:

SI 1: Effect of DMSO cryopreservant on electrooxidation

SI 2: Basis for model water matrices

SI 3: Contribution of particle separation to the EC-EO treatment train

SI 4: Effect of total charge loading on bacteriophage removal

SI 5: Reactor performance during the EC-EO process

SI 6: Iron generation and residuals through the EC-EO process

SI 1: Effect of DMSO cryopreservant on electrooxidation

As shown in Figure S1, dimethyl sulfoxide (DMSO) inhibited bacteriophage inactivation due to boron-doped diamond (BDD) electrooxidation (EO). For this reason, viruses were not stored with cryopreservant. Viruses were stored at -20° C and used within 2 months of propagation to prevent significant loss of titer.

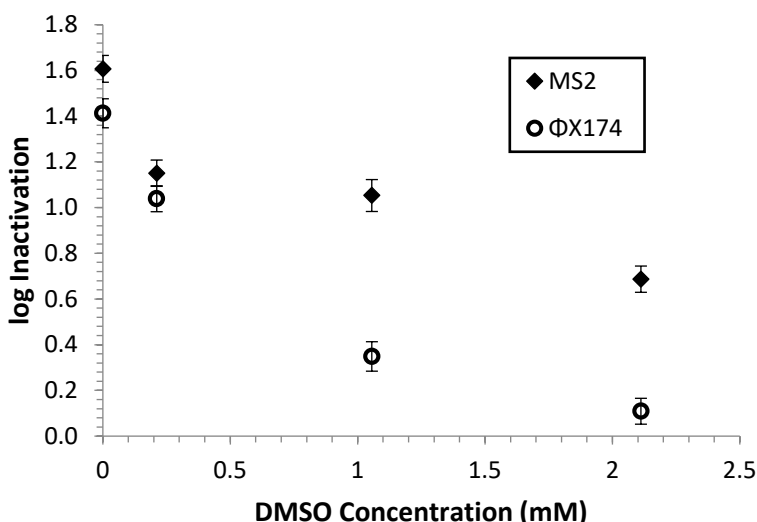


Figure S1. Effect of DMSO on removal of bacteriophages MS2 and ΦX174 due to electrooxidation (100 mA, 5 min) in 2.1 mM NaHCO₃. Error bars represent ± 1 standard error of mean plaque count ($n = 10$) for single tests.

SI 2: Basis for model water matrices

The four model waters used in this study (Table S1) were based on empirical values for water at four sites. Lake Michigan model water was based on median water parameters of Milwaukee Water Works source water in 2016 (Milwaukee Water Works, 2017). For Mississippi River model water, water quality data for United States Geological Survey (USGS) site 05288500 (Mississippi River at Hwy. 610 in Brooklyn Park, MN) was accessed via the USGS National Water Information System (NWIS) web interface (USGS, 2006). This sampling site was chosen based on breadth of water quality data and location in the upper Midwest US, similar to the other waters evaluated. Median values of water quality data ranging from 1996 to 2006 were used as the basis for Mississippi River model water. Dolomite Aquifer model water was a composite of shallow aquifer data from Kewaunee and Waukesha Counties, WI (Bonness and Masarik, 2014; Waukesha Water Utility, 2002). Sandstone Aquifer model water was based on deep aquifer data from Waukesha, WI (Waukesha Water Utility, 2002).

Reagent-grade KCl was added to achieve target chloride levels. Reagent-grade NaHCO₃ was then added to achieve target conductivity and approximate alkalinity. Test water pH was adjusted with H₂SO₄ to add sulfates found at the ppm level in environmental waters. A2 test dust and humic acid sodium salt were added to increase turbidity and natural organic matter (NOM), respectively. Hardness was not included in test water formulations because adding soluble CaCl₂ or MgCl₂ salt would often result in chloride concentrations many times greater than target levels.

Table S1. Empirical water quality data used to formulate model waters used in this study. Mississippi River data represents the median of water quality measurements between 1996 and 2006. Kewaunee groundwater data represents the median of water quality measurements in 10 wells in Lincoln Township, Kewaunee County.

Water Source	Associated Model Water	Conductivity ($\mu\text{S}/\text{cm}$)	Alkalinity (mg/L as CaCO_3)	Hardness (mg/L as CaCO_3)	Total Organic Carbon (mg/L)	Chloride (mg/L)	Sodium (mg/L)	pH	Turbidity (NTU)	Sulfate (mg/L)	Source
Lake Michigan	Lake Michigan	303	118	137	1.9	12.6	8.65	8.25	1	21.9	(Milwaukee Water Works, 2017)
Mississippi River	Mississippi River	359	162	180	8.65	11	7.7	8.1	30	13	(USGS, 2006)
Waukesha groundwater	Sandstone Aquifer	484 (300 mg/L TDS)	220	250		4.1	40	7.5			(Waukesha Water Utility, 2002)
Kewaunee groundwater	Dolomite Aquifer	774.5	323	413		28.25		7.82		28.25	(Bonness and Masarik, 2014)
Waukesha groundwater	Dolomite Aquifer	871 - 758 (540 - 470 mg/L TDS)	320	420		115	41.5	7.3			(Waukesha Water Utility, 2002)

SI 3: Contribution of particle separation to the EC-EO treatment train

Figure S2 shows the contribution of three different treatment processes on the reduction of the bacteriophages using boron-doped diamond (BDD) electrodes for electrooxidation (EO): 1) EO only without electrocoagulation (EC) pretreatment, 2) EC with a post-particle filtration step, and 3) EC pretreatment without particle separation.

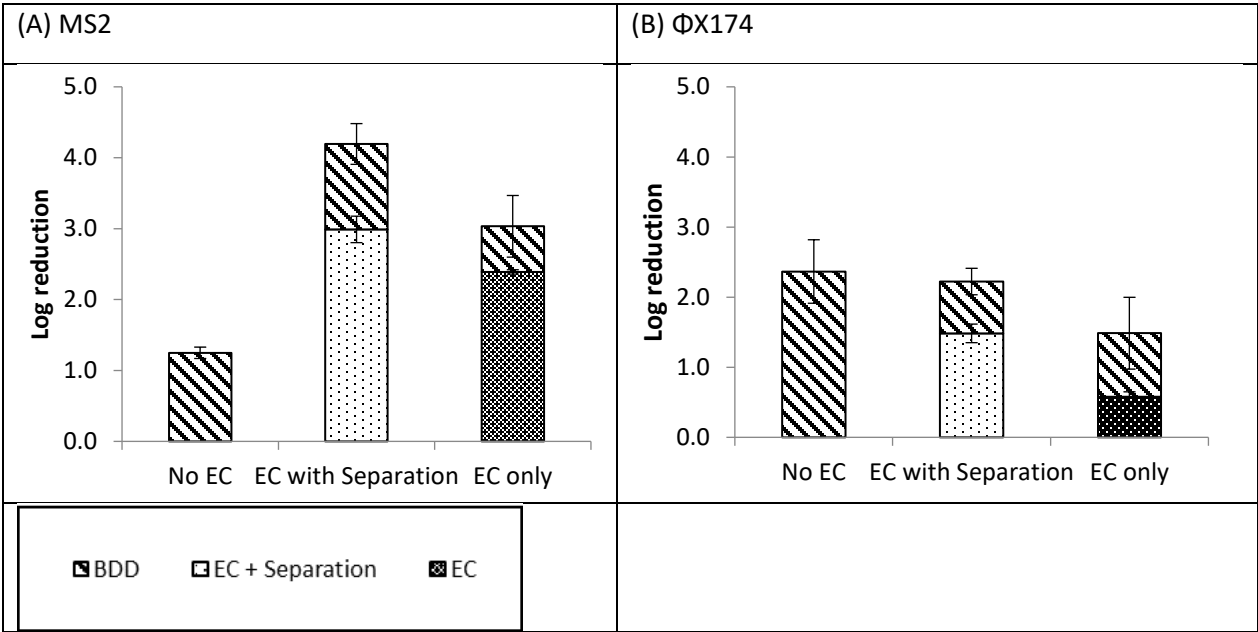
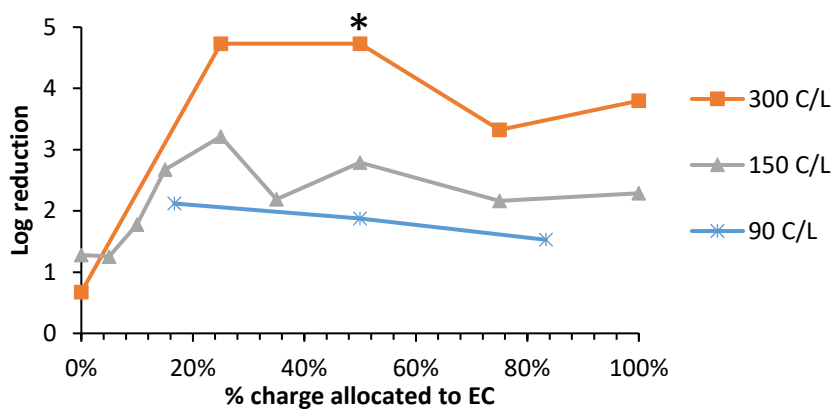


Figure S2. The effect of three treatment processes on the reduction of bacteriophages (A) MS2 and (B) ΦX174 by boron-doped diamond (BDD) electrooxidation: EO only (No EC), iron electrocoagulation followed by particle separation using a Whatman 114 filter (EC with Separation), and iron electrocoagulation with no particle separation (EC only). Particle separation after electrocoagulation improved overall virus reduction compared to electrocoagulation alone. Tests were conducted in 2.1 mM NaHCO₃, pH 7. Each data point represents the mean values of triplicate tests with ±1 standard error shown by the error bars.

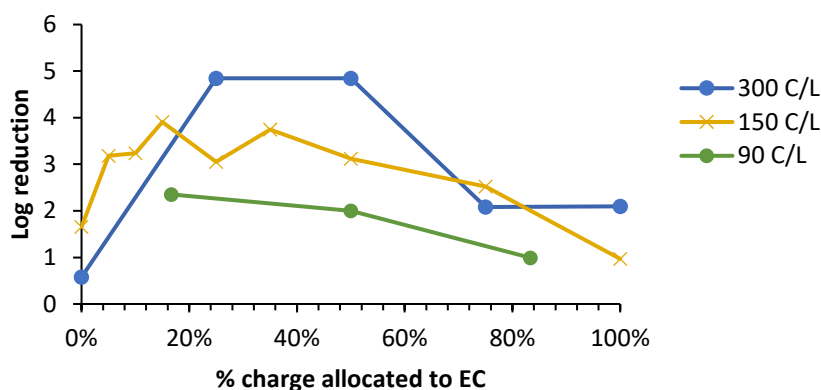
SI 4: Effect of total charge loading on bacteriophage removal

Three charge loadings (300, 150, and 90 C/L) were tested in Lake Michigan model water to determine an appropriate operating current for charge distribution tests in various model waters (Figure S3). Bacteriophage reduction using the 300 C/L electrocoagulation-electrooxidation (EC-EO) process exceeded the 4-log removal requirement set by the U.S. Environmental Protection Agency’s (EPA) Surface Water Treatment Rule, and was thus used for all subsequent tests.

(A) MS2



*
(B) ΦX174



* *
Figure S3. Reduction of bacteriophages (A) MS2 and (B) ΦX174 showing the effect of total charge on charge distribution between electrocoagulation (EC) and electrooxidation (EO). Tests were performed in the Lake Michigan model water. The * symbol indicates virus removal beyond the countable limit.

SI 5: Reactor performance during the EC-EO process

During sequential EC-EO treatment, pH increased on average 0.41 ± 0.25 pH units, as shown in Figure S4. For Lake Michigan and Mississippi River model surface waters, the change in pH was positively correlated ($p = 8.2 \times 10^{-5}$; $p = 1.9 \times 10^{-5}$, respectively) with increasing charge allocation to EC rather than EO. EC can increase the pH of solution due to the reduction of water at the cathode producing more hydroxide ions than are incorporated into iron precipitates (Dubrawski and Mohseni, 2013). Sandstone Aquifer and Dolomite Aquifer model groundwaters were not significantly correlated with charge allocation to one process over another.

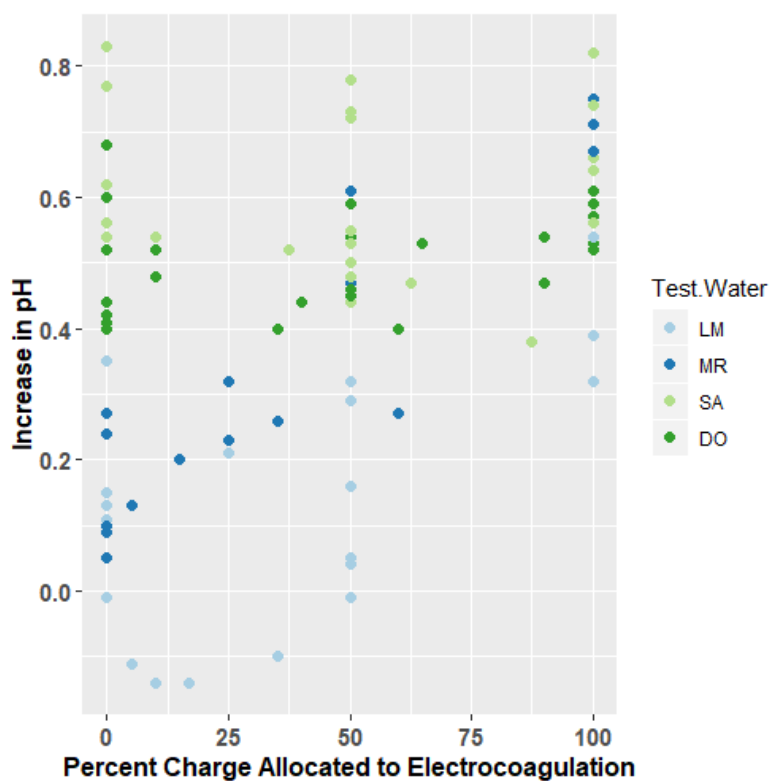


Figure S4. Increase in pH as a function of the percent of a constant charge loading (150 C/L) allocated between electrocoagulation (EC) and electrooxidation (EO). LM = Lake Michigan, MR = Mississippi River, SA = Sandstone Aquifer, and DO = Dolomite Aquifer model waters.

Figure S5 shows the energy density (kWh/m^3 , or energy input normalized to the reactor volume) required by each of the individual processes in the EC-EO treatment train. For the batch reactors used in this study, the energy required at a given current was approximately the same for EC and EO. Therefore, the percent of charge allocated to each process roughly mapped to the percent energy allocated. However, virus mitigation was related to charge allocation so that the results could be generalized to other EC and EO reactors. At 50% charge allocation, applied potentials were lowest due to even distribution of current; greater allocation to either EC or EO resulted in greater energy density due to exponentially increasing potential with increased current. Energy density at 50% charge allocation ranged from 0.12 to 0.41 kWh/m^3 per process (or 0.31 to 0.79 kWh/m^3 for the entire train). For perspective, most conventional drinking water treatment processes operate at $\leq 0.1 \text{ kWh/m}^3$ (e.g., the energy consumption to provide a typical UV dose of 40 mJ/cm^2 ranges from approximately 0.003 to 0.025 kWh/m^3 (Crittenden et al., 2012; Howe et al., 2012)).

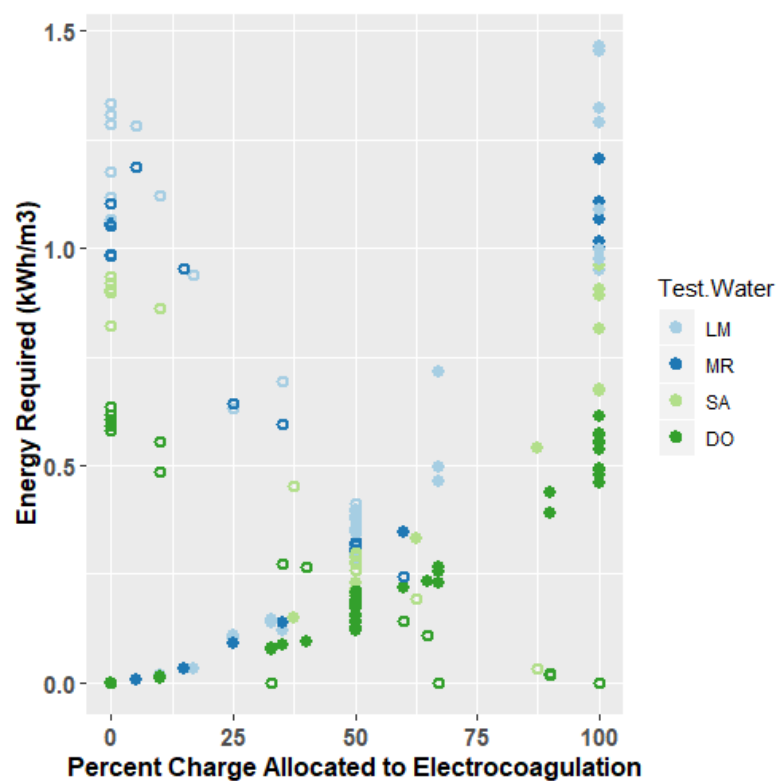


Figure S5. Energy required for electrocoagulation (filled circles) and electrooxidation (hollow circles) in a sequential electrocoagulation-electrooxidation treatment train. Energy usage was approximately symmetrical as a constant charge loading (150 C/L) was allocated from 100% electrooxidation (0% electrocoagulation) to 100% electrocoagulation. Energy requirements were inversely related to the conductivity of the model water, with decreasing energy from LM < MR < SA < DO. LM = Lake Michigan, MR = Mississippi River, SA = Sandstone Aquifer, and DO = Dolomite Aquifer model waters.

SI 6: Iron generation and residuals through the EC-EO process

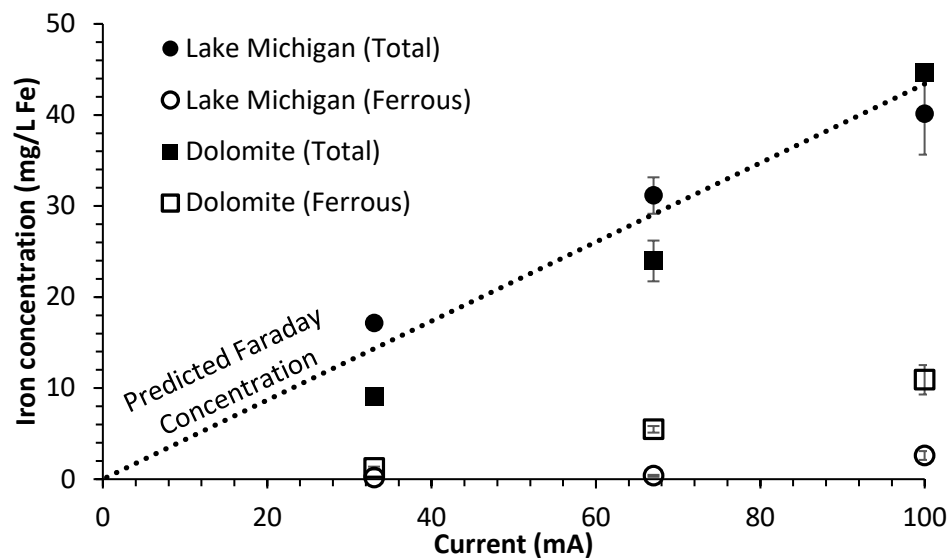


Figure S6. Total and ferrous iron generation by electrocoagulation (EC) as a function of current. Iron was generated by EC for 5 minutes in low-chloride, high-dissolved oxygen (DO) Lake Michigan model water and high-chloride, low-DO Dolomite Aquifer model water. In both model waters, total iron was generated at high (94-99%) Faraday efficiency. Ferrous iron residual increased with current and was greater in the low-DO Dolomite Aquifer water. The rate of ferrous iron oxidation is proportional to the DO concentration (Stumm and Lee, 1961).

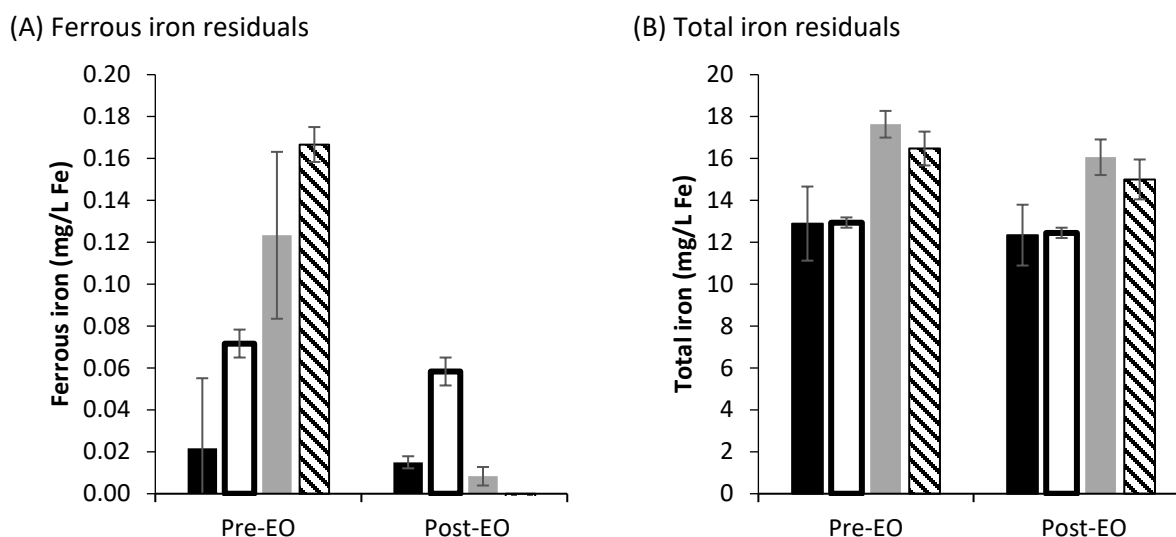


Figure S7. Total (A) and ferrous (B) iron residuals before and after electrooxidation (EO). Note the different scales of the y-axes. Iron concentrations were measured after coarse filtration with Whatman 114 filters. Pre-EO ferrous iron residuals were in the inhibitory range for EO, as shown in Figure 4. While total iron residuals remained high (~12 – 16 mg/L Fe) after final filtration (post-EO), post-EO ferrous iron concentrations were less than 0.02 mg/L Fe in all model waters except Mississippi River water. Natural organic matter binds ferrous iron and prevents oxidation to the ferric state. These results indicate that a post-treatment stage is required for decreasing iron residuals, and EO may increase the effectiveness of iron removal by oxidizing ferrous iron to less soluble ferric iron.

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